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ACCEPTED MANUSCRIPT Multiferroic Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O₃ perovskite: magnetic and thermodynamic properties

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Abstract

thermodynamic properties of polycrystalline Magnetic and multiferroic Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O₃ synthesized under high-pressure and high-temperature conditions are reported. Magnetic properties were studied using a SQUID magnetometer technique over the temperature range of 5 - 300 K in magnetic fields up to H = 10 kOe. The field dependent magnetization M(H) was measured in magnetic fields up to 50 kOe at different temperatures up to 230 K after zero-field cooling procedure. A long-range magnetic ordering of the AFM type with a weak FM contribution occurs below the Néel temperature $T_N \sim 237$ K. Magnetic hysteresis loops taken below T_N show a huge coercive field up to $H_c \sim 10$ kOe. A strong effect of magnetic field on the magnetic properties of the compound has been found. Derivative of the initial magnetization curves demonstrates a temperature-dependent anomaly in fields of H = 15 - 25 kOe. Besides, an anomaly of the temperature dependent zero-field cooled magnetization measured in magnetic fields of 6 - 7 kOe has been found. Origin of both anomalies is associated with inhomogeneous magnetic state of the compound. The heat capacity has been measured from 2 K up to room temperature and a significant contribution from the magnon excitations at low temperatures has been detected. From the low-temperature heat capacity, an anisotropy gap of the magnon modes of the order 3.7 meV and Debye temperature $T_D = 189$ K have been determined.

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1. Introduction

Within the broad class of materials available today, multiferroics are considered as a most promising basis for developing novel devices. This is due to the fact, that their physical properties are sensitive to the changes in external factors, namely temperature, pressure, electric and magnetic fields. Coupling between electronic and magnetic subsystems in multiferroic materials has attracted a particularly considerable attention in recent several years [1, 2, 3, 4]. These materials combine spontaneous magnetic and polar order parameters offering a unique opportunity of their effective cross-control.

In many multiferroics, a spin-driven electric polarization is induced by inverse Dzyaloshinskii-Moriya effect imposed by antisymmetric exchange interactions [1]. The Dzyaloshinskii-Moriya interaction (DMI) originates from the relativistic spin-orbit coupling, and in low-symmetry crystal structures without inversion centers it gives rise to antisymmetric magnetic exchange. DMI plays an important role in the formation of inhomogeneous spin structures such as long-wavelength spirals, vortex states, and skyrmion textures [5]. These interactions are also responsible for appearance of a weak ferromagnetism in some antiferromagnets including the important class of materials derived from the room-temperature multiferroic BiFeO₃ [3]. In addition, antisymmetric exchange is a source of magnetic anisotropy in many magnetically ordered compounds which removes degeneracy and selects specific ordered states in some geometrically frustrated spin systems [6, 7].

BiFeO₃ demonstrates a long-range antiferromagnetic (AFM) ordering below $T_N = 635$ K with no further indication of FM (FM) or glass contributions down to 2 K [8]. A dilution of magnetic Fe⁺³ ions with non-magnetic Sc⁺³ leads to the appearance of a new multiferroic phase [9]. A metastable perovskite BiFe_{0.5}Sc_{0.5}O₃ synthesized under high-pressure and high-temperature conditions was obtained in two different polymorphs, antipolar Pnma and polar Ima2, depending on heating/cooling history. The substitution of iron by scandium results in the decrease of the Néel temperature of the compound and appearance of weak ferromagnetism below T_N. Below T_N~220 K, both polymorphs exhibit a long-range AFM ordering with a weak FM component driven by DMI. It should be noticed that the polar modification of BiFe_{0.5}Sc_{0.5}O₃ with Ima2 symmetry is a new type of distorted perovskite structure which combines polarization and magnetization at high temperature ~ 220 K [9].

Metastable $Bi_{1-x}La_xFe_{0.5}Sc_{0.5}O_3$ (0.00 $\le x \le 0.80$) perovskites are the new examples of single-phase multiferroics which were recently obtained under high-pressure conditions [10, 11]. The system demonstrates a rich phase diagram. Three consecutive phases with different crystal structures appear as the lanthanum content is increased: the as-prepared phase at $x \le 0.05$ is an

antipolar Pnma [9] while an incommensurately modulated phase with the Imma(00 γ)s00 superspace group [10] is observed for $0.10 \le x \le 0.30$ and a non-polar Pnma phase [11] is stable at $x \ge 0.35$.

Our recent temperature-dependent static magnetic measurements revealed a long-range magnetic ordering of the antiferromagnetic type with a weak ferromagnetic contribution below $T_N \sim 206-260$ K for $Bi_{1-x}La_xFe_{0.5}Sc_{0.5}O_3$ ($0.00 \le x \le 0.80$) perovskites. The ferromagnetic contribution increases with decreasing temperature down to 5 K. Below T_N , field-dependent magnetization measurements showed well-defined hysteresis loops, which are typical of canted antiferromagnets [10, 11, 12]. No saturation of magnetization is observed up to H = 50 kOe.

The Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O₃ perovskite is close to the compositional transition between the antipolar Imma and the non-polar Pnma phases. Boundary compounds are of particular interest because may have enhanced electronic and magnetic properties [13]. Such compounds often represent a mixture of coexisting magnetic phases, which gives rise to unusual phenomena, such as exchange bias phenomenon and slow magnetic relaxation [14, 15]. Therefore, a study of the boundary compound Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O₃ is of a high interest. According to the previous neutron diffraction study, Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O₃ compound crystallizes into distorted single phase perovskite structure with the orthorhombic Pnma ($\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$) symmetry. The Neel temperature of Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O₃ was estimated as T_N ~ 220 K, below which the compound demonstrates a long-range magnetic ordering of antiferromagnetic G-type with a weak ferromagnetic contribution driven by the antisymmetric exchange [11].

The present study is aimed at the magnetic and heat capacity characterization of the $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ perovskite. The obtained results are discussed in terms of possible nano-scale magnetic phase coexistence in this material.

2. Experimental details

In order to achieve the most homogeneous and single-phase ceramics, the $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ precursor was prepared via a sol-gel combustion route using nitrates of the respective metals. The appropriate volumes of the nitrates were mixed together in a beaker and complexing agent (citric acid monohydrate) was then added to the above solution in different molar ratios according to propellant chemistry. The resulted solution was mixed for 1 h at 333 K and then concentrated by evaporation of solvent at 373 K until it turned into a brown viscous gel. Finally, the resulted gel was heated up to about 670 K to initiate combustion reaction. The obtained ultra-fine powders were calcined in air at 870 K for 2 h to remove organic remains.

High pressure was generated using an anvil press DO-138A with a press capacity up to 6300 kN. The ceramic samples were sintered at 6 GPa and 1020 K for 1 min.

X-ray diffraction study of the powdered samples performed using a PANalytical XPert MPD PRO diffractometer (Ni-filtered Cu K α radiation) at room temperature has shown a single phase perovskite structure of the obtained Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O₃ ceramics.

Magnetic properties of the ceramics were studied using a SQUID magnetometer technique (Quantum Design MPMS-3) between 5 K and 300 K in an applied fields up to 10 kOe under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. Isothermal magnetization measurements were performed between – 50 kOe and 50 kOe between 5 K and 230 K.

Magnetic relaxation measurements have been done using a home-made SQUID magnetometer, where the magnetic field H = 10 mT was frozen and controlled by a Hall sensor to avoid an effect of any uncontrolled residual field.

Heat capacity C(T) measurements were made using Quantum Design Physical Properties Measurement System (PPMS) in the 3 - 320 K temperature range in magnetic fields up to 6 kOe.

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3. Results and discussions

3.1. Magnetic properties of the Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O₃

In the present study by means of dc and ac magnetometry technique the Néel temperature of $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ compound is determined as $T_N \sim 237$ K, below which a weak ferromagnetic component develops. Temperature dependent real part, χ' , of the ac magnetic susceptibility has an anomaly at ~ 237 K which is associated with the Néel temperature. The ferromagnetic contribution increases with decreasing temperature down to 5 K (Fig. 1a). The temperature dependent zero-field-cooled magnetization taken in low magnetic field of H = 0.02 kOe has an anomaly in the temperature range close to 100 K which suggests a coexistence of two different magnetic phases (Fig. 1a, the insert). It is in a good agreement with a naturally phase separated state of the compounds, which are close to the compositional transition of the phase diagrams. Two or more phases are coexistent in such boundary compounds [13]. However, a careful examination of the neutron diffraction patterns collected between 1.5 and 300K (see Ref. [11] for details of the neutron diffraction experiment) did not reveal any evidence of the phase coexistence, indicating that the possible inhomogeneity takes place in a nano-scale level.

ZFC and FC magnetization curves measured in low magnetic fields are strongly different which is associated with anisotropy of the compound. The difference vanishes in magnetic field of about 10 kOe.



Fig. 1. (a) Temperature dependent dc magnetic moment measured in magnetic field of 0.02 and 0.1 kOe after zero field cooling (ZFC) and field cooling (FC) procedures. (b) Temperature dependent real part, χ' , of the dynamic magnetic susceptibility taken with ac magnetic field of 1.5 Oe and at measuring frequencies of 1.7 – 976 Hz. The $\chi'(T)$ dependences have an anomaly at ~ 237 K which is associated with the Néel temperature.

Magnetic hysteresis loops taken below T_N are characterized by a huge coercive field up to $H_c \sim 10$ kOe (Fig. 2, the insert). It can be considered as an indirect evidence of the magnetic phase segregated state of $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ compound as well.



Fig. 2. (Upper panel). Initial magnetization curves measured after zero field cooling procedure at different temperatures. (The insert) Magnetic hysteresis loops measured after zero field cooling procedure at temperatures 5, 50, 150, and 230 K (denoted as a, c, e and f, respectively). (Lower panel). Derivative of the initial magnetization. Letters denote the temperatures 5, 25, 50, 100, 150, and 230 K (a, b, c, d, e and f, respectively).

A strong magnetic field effect on the magnetic properties of $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ was found. Let us consider the initial magnetization curves, M(H), taken at fixed temperatures below T_N after zero field cooling process (Fig. 2, upper panel). At first sight, they look like almost straight lines. Nevertheless, analysis of the derivatives of the magnetization curves (Fig. 2, down panel) has shown their non-linear nature. Since magnetic moment of AFM compounds has the linear magnetic field dependence, no peculiarities of the $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ magnetic field derivative were expected. However, in our case, the derivative curves of the initial magnetization demonstrate a temperature-dependent anomaly (sort of a hill) in fields of H = 15 – 25 kOe, which indicates a change in slope of the M(H) curves. The anomaly shifts to the lower magnetic field side with increase of temperature and disappears above the Néel temperature. The anomaly is associated with a magnetic phase transformation and needs to be further studied.

An unexpected anomaly of the temperature dependent ZFC magnetization M(T) of $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ has been found with varying the measuring magnetic field (Fig. 3). ZFC magnetization of the compound taken in relatively low magnetic fields of H = 0.1 –3 kOe is smooth with no evidence of low-temperature magnetic phase transformation. The ZFC M(T) curves taken in magnetic fields of H = 6 – 7 kOe demonstrate a clear hill-like anomaly at temperature T_g which is slightly below T_N ~ 237 K. The amplitude of the anomaly reaches its maximum at H ~ 7 kOe. The anomaly vanishes in high magnetic fields above H ~ 10 kOe. The anomaly found is connected with a change of the magnetic state of the compound in relatively low magnetic fields, and is observed only when the compound is zero field cooled, which permits spins to align along their natural directions. At the same time, field-cooled M(T) curves demonstrate no anomaly. It means that cooling the compound in measuring magnetic field before the FC magnetization measuring procedure, which is done on heating of the sample, forms a preferred direction of spins, and suppresses the anomaly. It is associated with extremely high sensitivity of the compound to the applied magnetic field.



Fig. 3. Temperature dependent magnetic moment measured in magnetic field of 3 - 10 kOe in zero field cooled (ZFC) and field cooled (FC) modes.

A slow time relaxation process in the zero-field-cooled magnetization of $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ has been experimentally revealed (Fig. 4). The M(t) data were collected after zero field cooling at 5 K and 125 K as a function of time. At 125 K there is a continuous increase of the magnetization even after 40 minutes, during which about 32.2 % of the FC magnetization

(H = 100 Oe) were reached. The long-time relaxation behavior observed is associated with the tendency of spins to align in the applied magnetic field.

The time dependent magnetization M(t) measured at 5 K is very unusual; it suggests presence of two competing relaxation mechanisms. The M(t) shows a positive slope at the beginning (~ 8 min) of the time run, indicating an enlargement of the FM contribution. The magnetization reaches its maximum after approximately 10 minutes and starts to decrease after approximately 15 minutes (Fig. 4). This curious peak of M(t) observed suggests a competition between at least two different low magnetic field relaxation processes, the "up" relaxation one and the "down" relaxation one. The "up" relaxation process dominates in the beginning; the "down" one dominates after about 15 min at this temperature. The nature of the "down" relaxation process is not quite clear so far and needs a particular study. It is presumably caused by the processes occurring on the interfaces between clusters with different magnetic nature, their thermally activated dynamics and non equilibrium magnetic state.



Fig. 4. Time dependent magnetizations for the ZFC cooled $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ perovskite immediately taken after applying magnetic field of H = 100 Oe at different temperatures.

It should be noticed that in our time dependent experiments the input and output time of the magnetic field in the solenoid is several tens of seconds, while the magnetic relaxation process does not finish even after about 40 minutes (Fig. 4). Slow relaxation processes are evident of a significant magnetic viscosity of the compound, implying a complex rearrangement of the magnetic subsystem associated with its heterogeneity and internal stresses.

For better understanding of a quasi equilibrium magnetic state of the studied $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ compound, a distribution of Fe and Sc atoms in the Fe/Sc sublattice was simulated by using of the Mersenne Twister [16] pseudorandom number generator. The analysis of the modeling showed that at a given chemical composition, almost all iron atoms (about 98%) form

a connected area. Hence, in this case the formation of separate groups of iron atoms (geometric clusters) is hardly possible. At the same time, if one takes into account the magnetic states of the iron atoms, it can lead to the possible formation of magnetic clusters in the $Bi_{1-x}La_xFe_{1-y}Sc_yO_3$ (x, y = 0..1) system.

3.2. Thermodynamic properties

The heat capacity of $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ measured between 2 K and 300 K is shown in Fig. 5. For better representation of the experimental data, C(T) vs T is shown. The C/T dependence reveals the characteristics of an insulating material. Applied magnetic fields up to 6 kOe do not affect the temperature dependent heat capacity in the whole temperature range studied. No anomalies of the C(T) behaviour indicating any magnetic phase transition below room temperature were found. At the first sight this contradicts the magnetic data and neutron diffraction data, according to which $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ demonstrates a long-range magnetic ordering below $T_N \sim 237$ K. For a closer look, we made a detailed analysis of the low-temperature data (Fig. 5, the inset). It was found that neither a pure T³ phonon term, nor an additional T³ term due to gapless magnons of an isotropic antiferromagnet, provide a satisfactory fit to the low-temperature heat capacity experimental data. The linear contribution of the free electrons γT is not present in the studied magnetic insulators. The best fit to the low temperature heat capacity is obtained using the sum of a T³ phonon contribution and of a gapped magnon contribution:

$$C(T) = C_{lat} + C_{mag} = A \cdot T^3 + B \cdot exp(-\Delta/T)$$

where C_{lat} , given by a Debye function in pure insulators, is the phonon contribution; C_{mag} is an exponential Einstein-like contribution due to gapped magnon modes; A, B and Δ are the fitting parameters [8]. From the low-temperature fit a Debye temperature, T_D of 189 K, and a magnetic anisotropy gap Δ of 42.8 K, corresponding to an energy of approximately 3.7 meV, have been obtained. The energy of the gap obtained agrees well with magnon excitations located between 2.2 and 4.2 meV found experimentally for parent BiFeO₃ perovskite by Raman scattering techniques [17]. The obtained value of the Debye temperature, T_D = 189 K, is much lower than the temperature of the AFM transformation T_N ~ 237 K found by magnetic experiments, which does not permit to see heat capacity anomaly in the vicinity of T_N.

The best fitting curve, the lattice and magnon contribution to the total heat capacity estimated from the fitting are shown in Fig. 6. Both contributions, C_{tat} and C_{mag} , have substantial weight and in the 8 – 20 K temperature range the phonons and the magnons approximately equally contribute to the heat capacity of Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O₃. It is in a good agreement with low-temperature heat capacity contributions for parent compound BiFeO₃ [8].

Below about 8 K the temperature dependent heat capacity of the studied compound strongly deviates from the canonical Debye-like behavior, increasing with the temperature decrease (Fig. 6). Such low temperature deviation may result from the linear electronic contribution or from the disordered or amorphous matter. In our case of the magnetic insulator, the electronic term is absent, and the low temperature deviation of the temperature dependent C/T^3 curve may be associated with disordering caused by the disordered regions in grain boundaries, domain walls or interfaces of coexistent magnetic phases. Such behavior is often obseved in complex perovskites [8].



Fig. 5. Temperature dependent heat capacity of $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ between 2 K and 300 K. The inset shows the low temperature region in an enlarged scale. The line represents fitting with a sum of a phonon-like T³ contribution and a gapped magnon contribution.



Fig. 6. The low-temperature heat capacity of $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ plotted as C/T³ vs. T. The experimental results have been fitted by a sum of phonon T³ contribution and a gapped magnon contribution, described by an Einstein-like exponential term with a constant gap.

4. Conclusions

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In summary, we have studied magnetic and thermodynamic properties of a new metastable multiferroic $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ perovskite, which is close to the compositional transition between the antipolar and the non-polar phases of the $Bi_{1-x}La_xFe_{0.5}Sc_{0.5}O_3$ phase diagram. A long-range magnetic ordering of the AFM type with a weak FM contribution takes place below the Néel temperature $T_N \sim 237$ K. Our detailed dc ZFC temperature and time dependent experiments have shown that the magnetic state of the compound is inhomogeneous, it rather represents a mixture of at least two nano-scale magnetic phases. Magnetic field dependent experiments confirm a magnetic phase segregated state of the compound which may be associated with a boundary position of the compound in the phase diagram. A strong magnetic field effect on the magnetic properties of the compound has been found.

Temperature dependent heat capacity below about 20 K temperature has been fitted by a sum of T³ phonon contribution and of a gapped magnon contribution. An anisotropy gap of the magnon modes of 42.8 K, corresponding to an energy of 3.7 meV and Debye temperature of 189 K have been obtained.

Acknowledgments

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Figure captions

Fig. 1. (a) Temperature dependent dc magnetic moment measured in magnetic field of 0.02 and 0.1 kOe after zero field cooling (ZFC) and field cooling (FC) procedures. (b) Temperature dependent real part, χ' , of the dynamic magnetic susceptibility taken with ac magnetic field of 1.5 Oe and at measuring frequencies of 1.7 – 976 Hz. The $\chi'(T)$ dependences have an anomaly at ~ 237 K which is associated with the Néel temperature.

Fig. 2. (Upper panel). Initial magnetization curves measured after zero field cooling procedure at different temperatures. (The insert) Magnetic hysteresis loops measured after zero field cooling procedure at temperatures 5, 50, 150, and 230 K (denoted as a, c, e and f, respectively). (Lower panel). Derivative of the initial magnetization. Letters denote the temperatures 5, 25, 50, 100, 150, and 230 K (a, b, c, d, e and f, respectively).

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Fig. 6. The low-temperature heat capacity of $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ plotted as C/T³ vs. T. The experimental results have been fitted by a sum of phonon T³ contribution and a gapped magnon contribution, described by an Einstein-like exponential term with a constant gap.

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Fig. 1. (Up panel) Temperature dependent dc magnetic moment measured in a magnetic field of 0.02 kOe after zero field cooling (ZFC) and field cooling (FC) procedures. (Down panel) Temperature dependent real part, χ' , of the dynamic magnetic susceptibility taken with ac magnetic field of 1.5 Oe and at measuring frequencies of 1.7 - 976 Hz. The $\chi'(T)$ dependences have an anomaly at ~ 237 K which is associated with the Néel temperature.

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Highlights

- A strong effect of magnetic field on the magnetic properties of the compound has been found.
- Derivative of the *initial* magnetization curves demonstrates a temperature-dependent anomaly in fields of H = 15 25 kOe.
- A long-range antiferromagnetic ordering with a weak ferromagnetic contribution occurs below the Néel temperature $T_N \sim 237$ K.
- Magnetic hysteresis loops taken below T_N show a huge coercive field up to $H_c \sim 10$ kOe.

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